X-ray Absorption Fine-Structure Spectroscopy Study of Charge/Discharge Dynamic Characteristic of $LiFePO_4$ Crystalline Structure in Lithium Ion Battery

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Lithium transition metal phosphates ($LiFePO_4$) with an order olivine structure have become of great interest as storage cathodes for rechargeable lithium ion batteries because of their low raw materials cost, environmental friendliness, excellent cyling capacity retention and safety. The energy density of $LiFePO_4$ is equal to that of presently used materials, based on the theoretical capacity of 170 mAh/g obtained from the Fe^{2+}/Fe^{3+} redox reaction at the potential of 3.4V vs, Li/Li^+. The key limitation of this material has been extremely low electronic conductivity (10^{-9} s/cm), which is much lower than the acceptable electronic conductivity (10^{-5} s/cm). Many studies have been made to find the means to improve the conductivity. In this work, cabon-coated $LiFePO_4$ synthesized by the solid-state method showed the discharge capacity of 140 mAh/g at the current rate of C/10 and maintained 1/2 retention at the rate as high as 12C rate, as shown in Fig. 1. It indicated that the electronic conductivity of pure $LiFePO_4$ could improve by the effective homogeneous carbon layer on the powders.

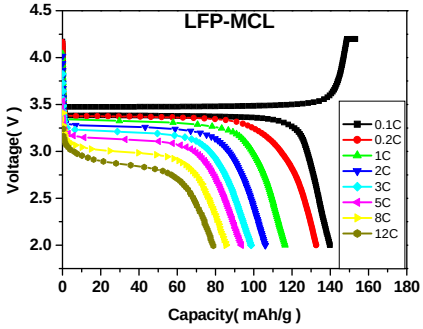

Figure 1. Charge/discharge profile of $LiFePO_4$ at different current rates.

In situ XAS experiments of metal K-edge were performed in transmission mode at beam line BL-17C at the National Synchrotron Radiation Research Center (NSRRC) at Hsinchu, Taiwan. Figure 2 showed the Fe K-edge XANES spectra of $LiFePO_4$ with different carbon-doping concentration compared with reference compounds (FeO and Fe_2O_3). From the detailed view of pre-edge region as shown in Fig.2b, the valence of Fe ion didn't change with the carbon concentrations, meaning that carbon elements occupy neither the lattice sites of transition metals nor the interstitial sites of olivine structure. The absorption edge positions of all $LiFePO_4$ samples were close to that of FeO, confirming that iron was present in the 2+ state. Moreover, the pre-edge region was assigned to 1s → 3d transitions, and its intensity depended on the geometry around Fe, which a weak intensity in this region indicated an octahedral coordination as opposed to the tetrahedral coordination from which a strong pre-edge intensity was found. From Fig. 2b, it could be seen that a presence of a strong pre-edge intensity showed in pure $LiFePO_4$ and the intensity became weaker in carbon-coated $LiFePO_4$ where Fe has been in the perfect octahedral symmetry.

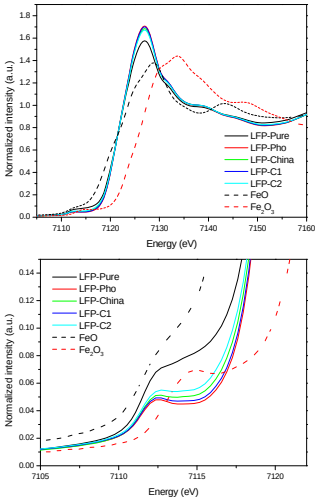

Figure 2. (a) The normalized Fe K-edge XANES and (b) the pre-edge region of (a) spectra.

Figure 3 showed the k^3-weighted Fourier transformed Fe K- edge EXAFS spectra for all samples. Two strong peaks were seen at the strat (at about 1.9 Å and 3.2 Å) and two weaker ones were observed at higher distances (at about 4 Å and 4.8 Å). The first two peaks of Fourier transform wrer attributed to the Fe-O bond and Fe-P bond and occurred at 0.1~0.2 Å shorted distances than those of pure $LiFePO_4$. Furthermore, the intensity of first two peaks were more intense, indicating the higher short-range ordering was achieved by carbon doping in the materials.

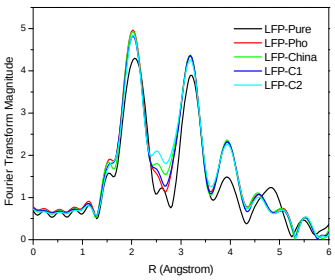

Figure 3. Radial structure function from the Fourier transform of the k3-weighted Fe K-edge EXAFS.